

# Modeling transport and deposition of contaminants to ecosystems of concern: a case study for the Laurentian Great Lakes

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Received 14 July 2003; received in revised form 11 August 2003

**“Capsule”:** *Transfer Efficiency is defined as a model-based measure of sources of POPs to the North American Great Lakes.*

## Abstract

Transfer efficiency (TE) is introduced as a model output that can be used to characterize the relative ability of chemicals to be transported in the environment and deposited to specific target ecosystems. We illustrate this concept by applying the Berkeley–Trent North American contaminant fate model (BETR North America) to identify organic chemicals with properties that result in efficient atmospheric transport and deposition to the Laurentian Great Lakes. By systematically applying the model to hypothetical organic chemicals that span a wide range of environmental partitioning properties, we identify combinations of properties that favor efficient transport and deposition to the Lakes. Five classes of chemicals are identified based on dominant transport and deposition pathways, and specific examples of chemicals in each class are identified and discussed. The role of vegetation in scavenging chemicals from the atmosphere is assessed, and found to have a negligible influence on transfer efficiency to the Great Lakes. Results indicate chemicals with octanol–water ( $K_{ow}$ ) and air–water ( $K_{aw}$ ) partition coefficients in the range of  $10^5$ – $10^7$  and  $10^{-4}$ – $10^{-1}$  combine efficient transport and deposition to the Great Lakes with potential for bioaccumulation in the aquatic food web once they are deposited. A method of estimating the time scale for atmospheric transport and deposition process is suggested, and the effects of degrading reactions in the atmosphere and meteorological conditions on transport efficiency of different classes of chemicals are discussed. In total, this approach provides a method of identifying chemicals that are subject to long-range transport and deposition to specific target ecosystems as a result of their partitioning and persistence characteristics. Supported by an appropriate contaminant fate model, the approach can be applied to any target ecosystem of concern.

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**Keywords:** POPs; Long range transport; Great lakes; BETR North America

## 1. Introduction

Potential for long-range transport in the environment is a characteristic of concern for anthropogenic chemicals, particularly for persistent organic pollutants. Some of these chemicals can be transported thousands of kilometers from their point of release, and in the extreme, are distributed throughout the global environment. Several generic evaluative models have been developed to assess the long-range transport potential of chemicals (Scheringer, 1996; Bennett et al., 1998; Beyer et al., 2000; Scheringer et al., 2001). The models

are designed for use in screening-level assessments to identify chemicals with potential for mobility in the environment over continental or global scales.

Existing evaluative models based on generic environmental conditions do not explicitly address the likelihood of chemicals being transported from source regions and deposited to a specific target ecosystem. Assessments of this type are required to estimate the relative contribution of different sources to the contaminant burden present in a particular ecosystem. The North American Great Lakes are an example of an ecosystem impacted by both local sources and by atmospheric deposition of contaminants transported over hundreds or thousands of kilometers (Eisenreich, 1981; Baker, 1997). Deposition rates for selected contaminants to the Great Lakes have been estimated since 1990 by the Integrated Atmospheric Deposition

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Network (IADN), based on data from a number of air monitoring sites in the Great Lakes Basin (Hoff et al., 1996). There is compelling evidence that contaminants that are used and released in other parts of the North American continent are transported and deposited to the Lakes. Chemicals such as DDT and toxaphene, which are currently banned or severely restricted in North America, continue to be deposited to the Lakes, possibly as a result of volatilization from distant soils contaminated by past usage.

Presumably, the efficiency with which a chemical is transported from an emission source and deposited to a target ecosystem is a function of (I) the properties of the chemical, specifically partitioning characteristics and reactivity, (II) the distance the chemical must travel to reach the target ecosystem, and (III) properties of the environment including meteorology and temperature conditions. Here, we present a general metric of potential for transport and deposition to target ecosystems, Transfer Efficiency (TE), and illustrate it using continental-scale transport and deposition to the Great Lakes as a case study.

We employ the Berkeley–Trent North American contaminant fate model [BETR North America] (Betts, 2001; MacLeod et al., 2001b; Woodfine et al., 2001; Dahl, 2002) to calculate transfer efficiency to the Great Lakes, but the techniques described could be adapted to any contaminant fate model that explicitly models inter-media transfer processes. The BETR model describes the North American environment as 24 ecological regions, as illustrated in Fig. 1. Within each region the fate of environmental contaminants is described using a seven-compartment fugacity model including a verti-

cally segmented atmosphere, vegetation, soil, freshwater, freshwater sediments and coastal water. Contaminants can be transported between adjacent regions of the model in the atmosphere and in flowing rivers and near-shore ocean currents.

## 2. Modeling the transport and deposition of persistent chemicals

The BETR North America model can be applied to describe steady-state continental contaminant fate for a constant release of chemical to the boundary layer of the atmosphere in any of the 24 regions of the model. At steady-state, inventories in each region and fluxes of contaminant between all regions and environmental compartments are constant such that emissions are balanced by removal processes for the entire continental environment. For each chemical emitted in each region, a transfer efficiency (TE) can be calculated as a percentage from the steady-state solution as:

$$TE = \frac{\text{rate of contaminant flux to the target ecosystem (kg/year)} \times 100}{\text{emission rate in the source region (kg/year)}}$$

The emission rate used as input to the BETR North America model represents primary emissions only. Re-volatilization of chemical from the terrestrial and aquatic surfaces is calculated by the mass balance equations in the model. The definition of emission rate used here is therefore different than that used by many atmospheric

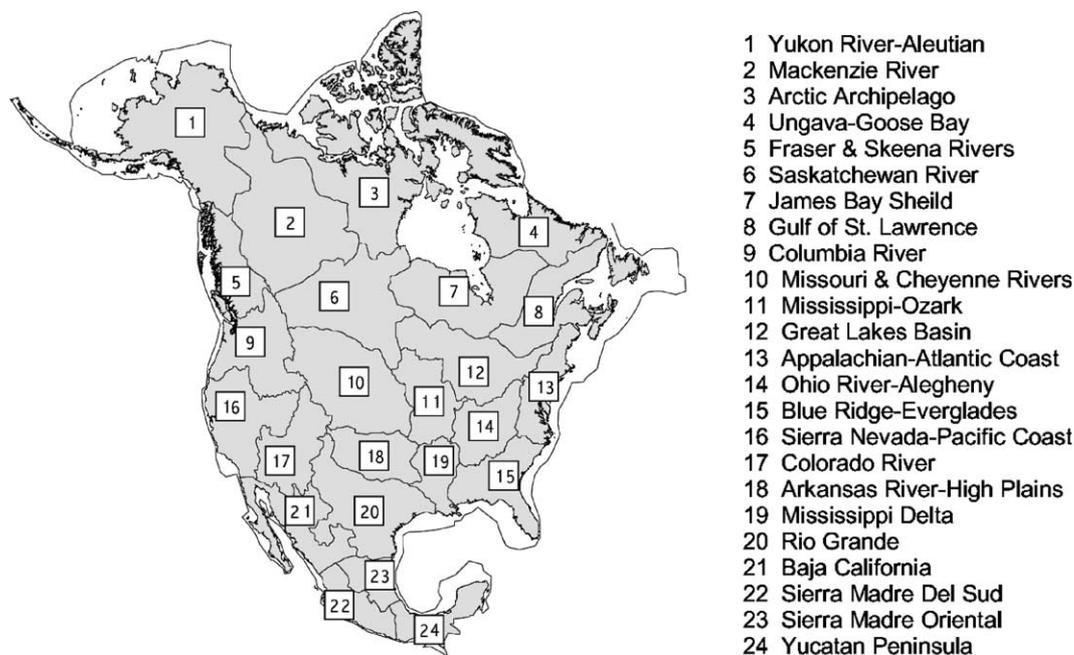


Fig. 1. Regional segmentation of the BETR North America model.

modelers, who use emissions to refer to the sum of primary emissions and volatilization.

Any individual compartment in the model, or a collection of compartments could represent the target ecosystem. In the case of the Great Lakes, we are primarily interested in direct deposition of contaminants from the atmosphere to the Lakes. We therefore define a Great Lakes Transfer Efficiency (GLTE) as:

$$\text{GLTE} = \frac{\text{rate of atmospheric deposition to Great Lakes (kg/year)} \times 100}{\text{emission rate to the atmosphere in the source region (kg/year)}}$$

where the Great Lakes are represented by the freshwater compartment in the model's Great Lakes Basin Region.

BETR North America has been applied to individual chemicals to describe their fate and transport in the continental environment and compared with monitoring data, as described by MacLeod et al. for toxaphene (MacLeod et al., 2001a). Although it is possible to simulate and compare specific chemicals according to transfer efficiency, we take a more general approach by simulating the behavior of hypothetical chemicals that span a wide range of partitioning properties typical of organic chemicals present in the environment and analyzing the continental scale fate of these chemicals as described by the model. The set of hypothetical chemicals is selected to represent the entire spectrum of potential environmental partitioning of non-ionizing organic chemicals. Combinations of octanol–water partition coefficients between  $10^0$  and  $10^{10}$  and air–water partition coefficients  $10^{-10}$  and  $10^5$  were used as inputs to the BETR North America model. This range of partitioning properties encompasses chemicals that partition almost exclusively to individual environmental media (i.e., air, water, soil or sediment), and multi-media chemicals that accumulate significantly in more than one compartment (Gouin et al., 2000; Wania, 2003). For simplicity, a conservative upper estimate of the GLTE for each combination of environmental partitioning characteristics was initially obtained by setting degradation half-lives in all environmental media to be arbitrarily long, i.e., exceeding  $10^9$  years. The effect of considering degrading reactions in the atmosphere is discussed later.

This approach is conceptually similar to the Arctic Amplification Contamination Potential (ACP) described by Wania (2003) and used to assess the relative potential for chemicals to accumulate in the Arctic environment. The current approach differs in that it applies the steady-state assumption to describe contaminant fate and transport over the North American continent, whereas ACP is derived from a dynamic model and therefore changes with the length of the model simulation.

Great Lakes Transfer Efficiencies for totally persistent chemicals from three regions of the BETR North

America model, the Great Lakes Basin, Mississippi Delta, and Sierra Madre Del Sur, are presented and discussed here in detail. When interpreting the results it proves convenient to classify chemicals into five groups with different partitioning properties and which experience different transport pathways, as shown in Fig. 2.

Class 1 substances are involatile and have low to intermediate hydrophobicity. Substances with these partitioning properties usually have polar functional groups and are quite soluble in water. They are efficiently scavenged from the atmosphere by dissolution in rain and absorption which is air-phase controlled. Examples are phenols and related substances such as catechol, guaiacol and Aldicarb. They are collectively referred to here as “polar involatiles”.

Class 2 substances are highly volatile and partition preferentially to the atmosphere under all environmental conditions. Once in the atmosphere, they are not efficiently re-deposited to the terrestrial surface. Examples are solvents such as chloroform, the freons, and short-chain hydrocarbons such as ethylene. They are referred to as “volatiles”.

Class 3 substances are involatile and highly hydrophobic. They are very sparingly soluble in water, but may volatilize from contaminated waters despite their low volatility. In the atmosphere, these substances are almost completely associated with atmospheric aerosols, and particle deposition processes control deposition from the atmosphere to the terrestrial surface. Examples are highly chlorinated polychlorodibenzo dioxins and furans and long chain polymers. They are termed “hydrophobic involatiles”.

Class 4 substances are intermediate in volatility and highly hydrophobic, with a Log  $K_{ow}$  exceeding 6. In the atmosphere, these substances partition appreciably to both the gas and aerosol phases, and the extent of partitioning is sensitive to temperature changes. Examples are intermediate and highly chlorinated polychlorinated biphenyls (PCBs). They are referred to as “hydrophobic semi-volatiles”.

Class 5 substances are intermediate in volatility and range in hydrophobicity up to a Log  $K_{ow}$  of about 6. They are significantly soluble in water. In the atmosphere they partition to a limited extent to aerosols. These substances are deposited from the atmosphere to surface waters by diffusive exchange in the gas phase. Examples are low to mid chlorination level PCBs and toxaphene. Here, they are termed “semi-volatiles”.

### 2.1. Transfer from within the Great Lakes Basin

Fig. 3 shows Great Lakes Transfer Efficiency for chemicals emitted to air in the Great Lakes Basin region. A line of constant octanol-air partition coefficient ( $K_{oa}$ ) of  $10^9$  is shown on the diagram, and indicates the boundary between chemicals that are primarily in the gas-

phase in the atmosphere (in the top left of the diagram) and those that are primarily associated with atmospheric particles (lower right of the diagram). Aerosol-air partitioning in the BETR North America model is

described using a regression with  $K_{oa}$  (Finizio et al., 1997).

Chemicals on the boundary between Class 1 and Class 5 are most effectively deposited from the atmo-

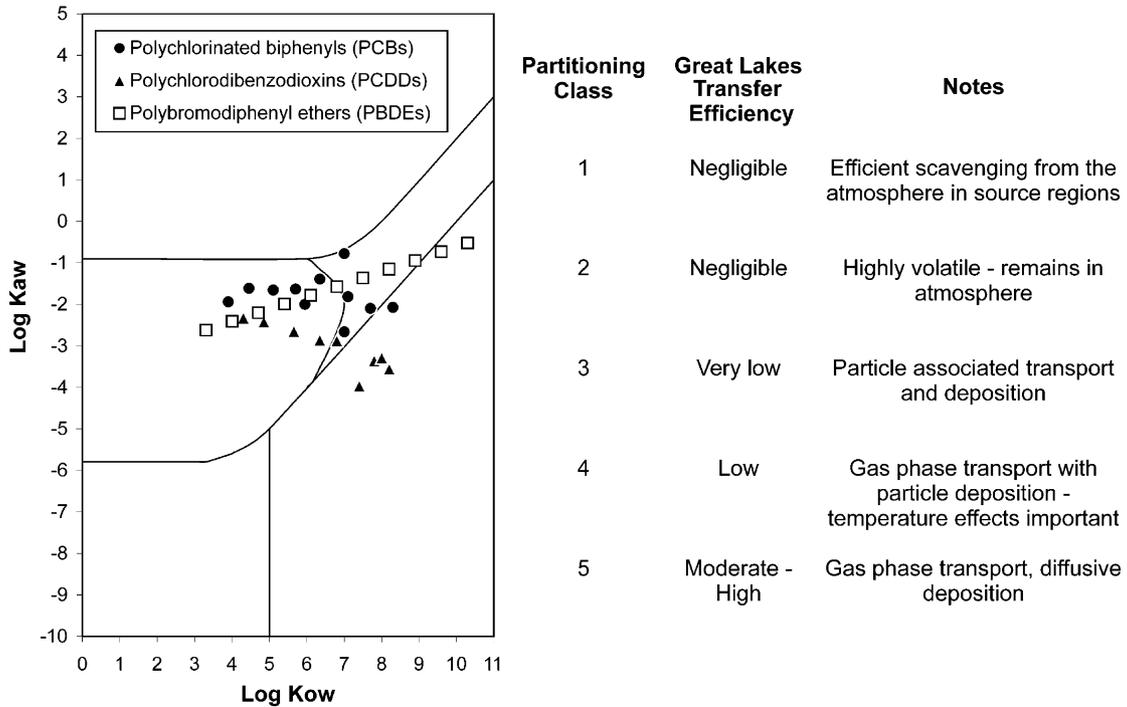


Fig. 2. General classification scheme for Great Lakes Transfer Efficiency.

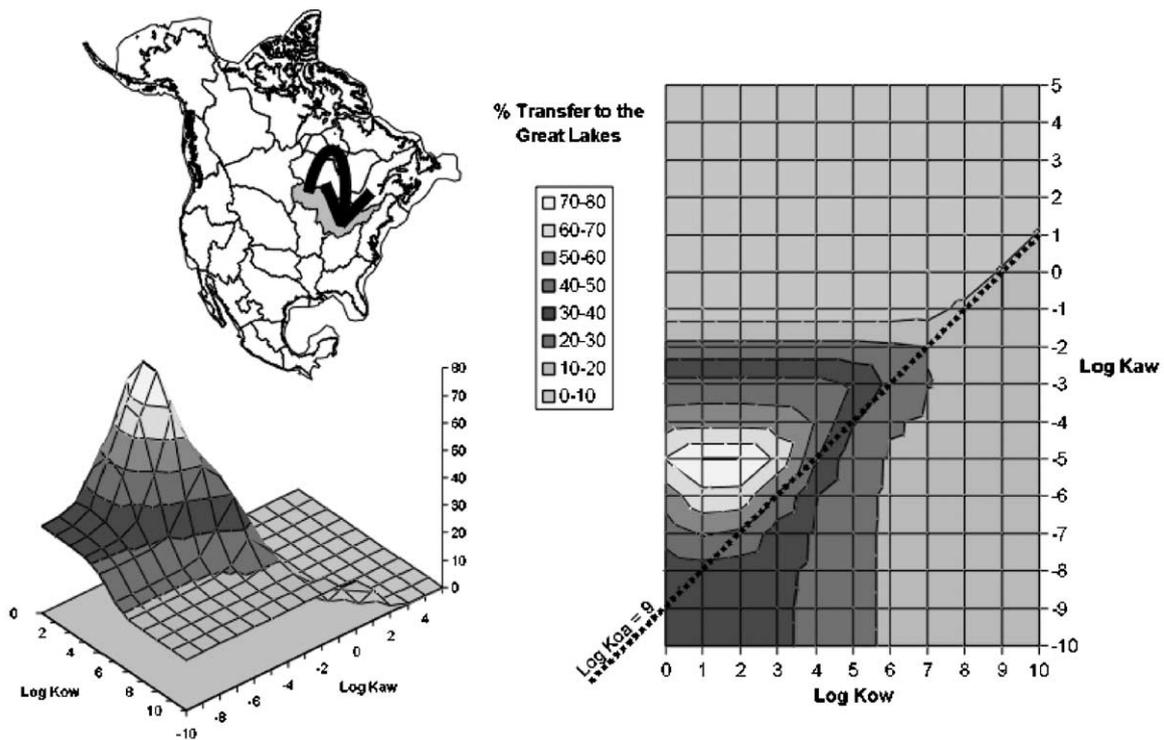


Fig. 3. Great Lakes Transfer Efficiency of persistent chemicals released to the atmosphere in the Great Lakes Basin Region. The maximum efficiency of atmospheric deposition of chemicals released in the Great Lakes Region is approximately 75%.

phere to the Lakes, with an efficiency of approximately 80%. In this range of partitioning properties, the dominant mechanism for removal from the atmosphere is dissolution in falling rain, which is very efficient at scavenging these chemicals from the air column. The Great Lakes cover only 30% of the total area of the Great Lakes Basin region, however efficiencies of up to 80% are possible because chemicals near the peak in the surface plot cycle from the terrestrial surface back to the atmosphere. The dominant pathway for re-emission is via root uptake by vegetation and subsequent volatilization back to the atmosphere, but evaporation from soil also occurs.

The plateau in the bottom left of the diagram (Class 1 chemicals) corresponds to a depositional efficiency of approximately 30%. These chemicals are deposited from the atmosphere by rain dissolution but are not re-emitted to the atmosphere from the terrestrial surface. Therefore the proportion of total deposition to surface water is approximately equal to the proportion of total area covered by fresh water in the Great Lakes Basin region.

Chemicals with  $\text{Log } K_{ow}$  less than 5 are not expected to significantly bioaccumulate in aquatic food chains. Transfer of these chemicals to the Great Lakes ecosystem is therefore not cause for the same degree of concern as chemicals with  $\text{Log } K_{ow}$  of 5 or greater. Hydrophobic involatile chemicals (Class 3) with high  $\text{Log } K_{ow}$  and low  $\text{Log } K_{aw}$  are deposited from the

atmosphere by wet and dry deposition on particles. This process is not as efficient as rain dissolution, and some chemical is removed from the region by advective transport in air. In addition, particle associated chemical deposited to the terrestrial surface is not recycled to the Lakes in this partitioning domain is approximately 20%.

Near the center of the diagram (hydrophobic Class 3 chemicals) there is a shoulder with depositional efficiency of about 40% that corresponds to diffusive deposition by semi-volatile chemicals that are not completely sorbed to particles in the atmosphere. This region of the partitioning diagram represents chemicals that have potential for bioaccumulation and are efficiently deposited to the Great Lakes. Toxaphene ( $\text{Log } K_{ow} = 5.5$ ,  $\text{Log } K_{aw} = -3.75$ ,  $\text{Log } K_{oa} = 9.25$ ) (Jantunen and Bidleman, 2000) is an example of a chemical in this partitioning domain.

## 2.2. Transfer to the Great Lakes from the Mississippi delta region

As indicated in Fig. 4, maximum transport efficiencies are in the range of 4% of atmospheric emissions to the Mississippi Delta region. Class 5 chemicals are most efficiently transported and deposited to the Great Lakes from this region. These chemicals are primarily in the gas phase in the atmosphere, and are deposited to the lakes by diffusion. Deposition to the Great Lakes is

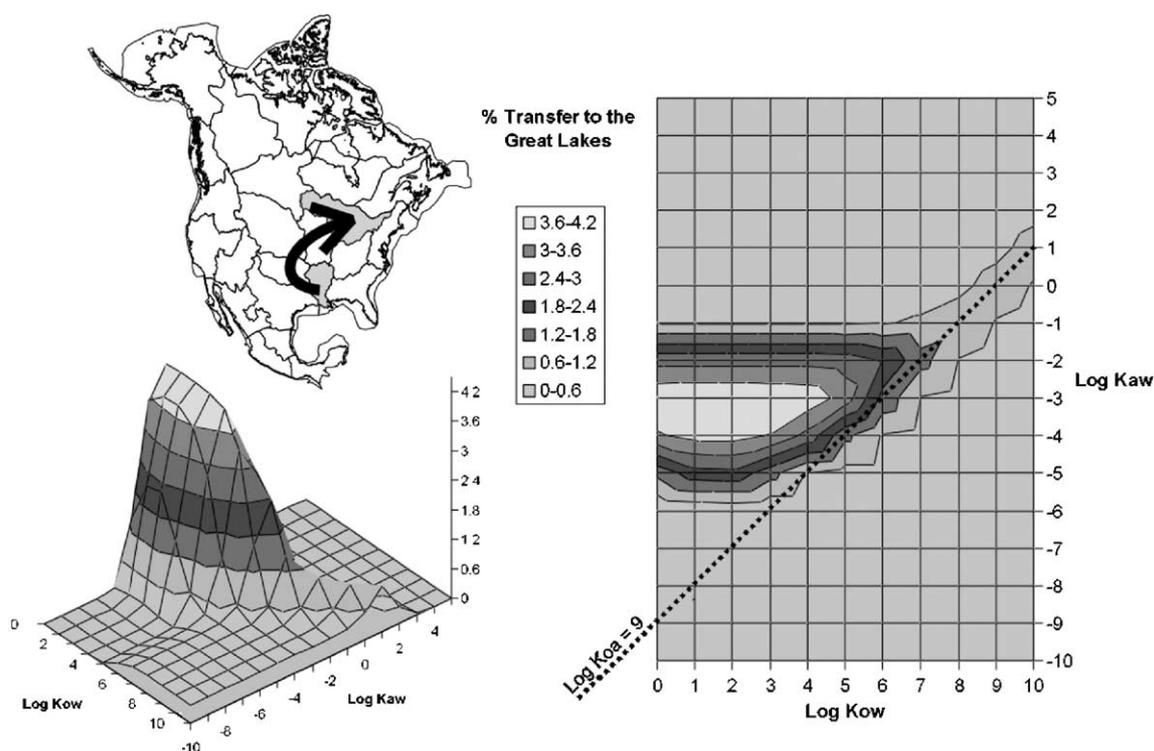


Fig. 4. Great Lakes Transfer Efficiency of persistent chemicals released to the atmosphere in the Mississippi Delta region, approximately 1500 km south of the Great Lakes. The maximum efficiency of transport and deposition is  $\sim 4\%$ .

efficient because of the large area of surface water available for diffusive transport.

At lower  $\text{Log } K_{aw}$ , Class 1 chemicals are removed from the atmosphere in the source region by rain dissolution. Transport and deposition with an efficiency of  $\sim 0.35\%$  is indicated for particle-associated hydrophobic involatiles (Class 3). These chemicals are deposited by wet and dry particle settling without regard to the surface to which they are depositing along the entire transport journey from the source region.

Among chemicals with  $\text{Log } K_{ow}$  exceeding 5, the most efficient transport and deposition to the Great Lakes are hydrophobic members of Class 5. These chemicals are deposited to the Lakes with an efficiency of up to 3% of atmospheric emissions in the Mississippi Delta region, primarily by diffusion which is relatively efficient because low  $\text{Log } K_{aw}$  makes resistance to diffusion on the air-side of the air-water interface the dominant resistance to transfer. As indicated previously, toxaphene has properties in this range; among chemicals with potential for bioaccumulation, toxaphene's combination of partitioning properties is among the most favorable for transport and deposition to the Great Lakes. DDT ( $\text{Log } K_{ow}=6.2$ ,  $\text{Log } K_{aw}=-3.3$ ,  $\text{Log } K_{oa}=9.5$ ) also lies on this shoulder of transport efficiency, combining a high  $\text{Log } K_{ow}$  with efficient transport and deposition.

Moving upward along the diagonal of constant  $\text{Log } K_{oa}=9$ , into Class 4 substances, diffusive exchange

between air and water is less favorable because water-side resistance begins to dominate total resistance to air-water diffusion. However, highly hydrophobic Class 4 chemicals can still be transported and deposited in the Great Lakes with efficiencies of 1%, with dry and wet particle deposition as the dominant mechanism for deposition. This route of removal from the atmosphere was not available in the more southerly regions because effective  $\text{Log } K_{oa}$  at environmental temperatures in these regions of the model does not sufficiently favor partitioning to aerosol particles in the atmosphere. Highly chlorinated PCBs are examples of chemicals that lie along this diagonal ( $\text{Log } K_{ow} \sim 7$ ,  $\text{Log } K_{aw} \sim -2$ ,  $\text{Log } K_{oa} \sim 9$ ).

### 2.3. Transfer to the Great Lakes from the Sierra Madre Del Sur region

Great Lakes Transfer Efficiencies from regions of the continent more distant than the Mississippi Delta follow a similar pattern of dependence on partitioning properties, with overall efficiencies reduced with increasing distance from the target ecosystem. Maximum transport efficiency from the Sierra Madre Del Sur region, on the western coast of Mexico, is only  $\sim 1\%$  of atmospheric emissions (Fig. 5). Chemicals with potential for bioaccumulation have peak efficiencies of 0.9% for those deposited by diffusion, and 0.25% for those deposited by wet and dry particle settling. Chemicals that are sor-

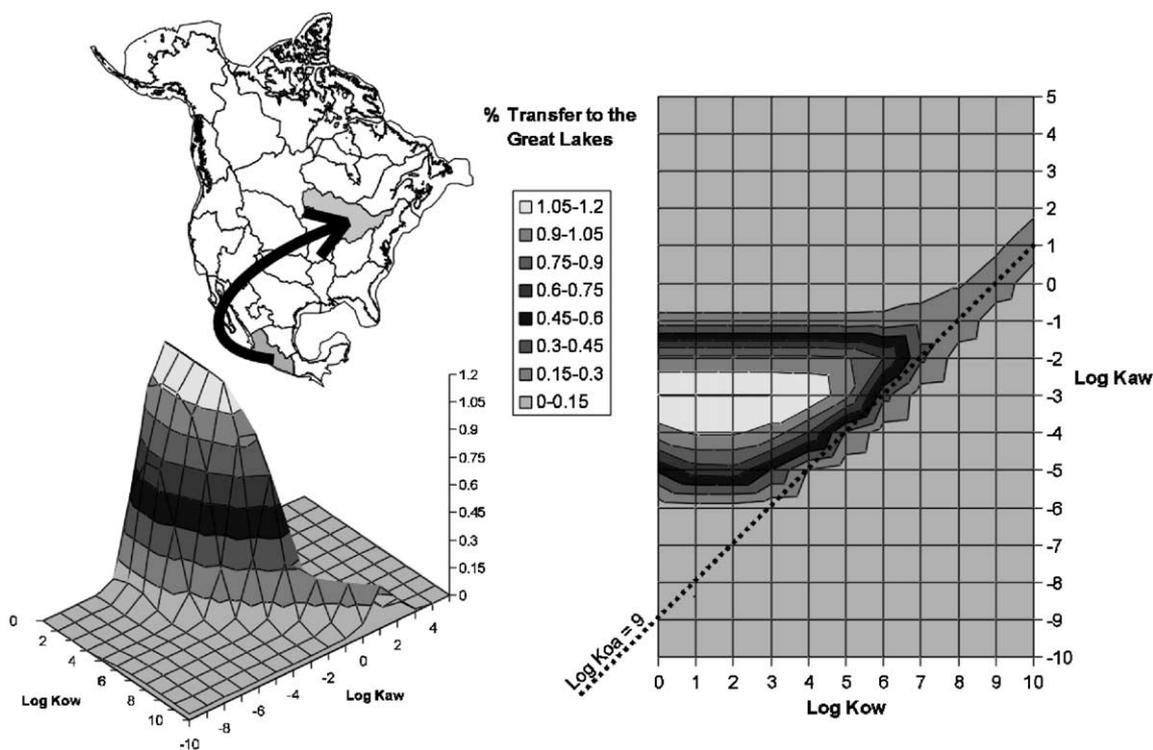


Fig. 5. Great Lakes Transfer Efficiency of persistent chemicals released to the atmosphere in the Sierra Madre Del Sur region, approximately 3500 km south-southeast of the Great Lakes Region. The maximum efficiency of transport and deposition is  $\sim 1\%$ .

bed to particles in the atmosphere at all relevant environmental temperatures (lower right portion of the diagram) are almost entirely deposited from the atmosphere before they reach the Great Lakes Basin.

### 3. The influence of vegetation on transport of contaminants

It is noteworthy that the combination of partitioning properties identified here as favoring transport and deposition to the Great Lakes Basin ( $\text{Log } K_{\text{oa}} \sim 9$  for chemicals with  $\text{Log } K_{\text{ow}} > 5$ ) overlaps with those that have been previously identified by Wania and McLachlan (Wania and McLachlan, 2001) as favoring scavenging from the atmosphere and deposition to the terrestrial surface by vegetation, particularly forest canopies. There is an apparent inconsistency between these two results, since scavenging by forests should retard transport in the atmosphere, however, close examination of the study by Wania and McLachlan reveals that results from these two studies are consistent.

Wania and McLachlan compare calculated atmospheric concentrations from a multi-media fate model with and without the inclusion of a vegetation compartment. They defined the ratio  $Q_A$  as the concentration of contaminant in air calculated in a scenario without a forest canopy compartment divided by the concentration assuming that half of the terrestrial surface area is covered by a mixed forest.  $Q_A$  is reported to have a maximum value of approximately 5 for chemicals with  $\text{Log } K_{\text{ow}} = 7$ ,  $\text{Log } K_{\text{aw}} = -2.5$  and  $\text{Log } K_{\text{oa}} = 9.5$ , implying deposition to the terrestrial surface via vegetation may significantly reduce atmospheric concentrations. However, in the Wania and McLachlan study the competing processes of advection that removes chemical from the atmosphere is understated relative to the advection conditions that prevail in the BETR North America model.

The focus of the Wania and McLachlan study was on the role of forests in increasing air to surface transfer, thus increasing surface concentrations and reducing those in air. Accordingly atmospheric concentrations in the inflowing and outflowing air were assumed to be equal thus there was no net loss by advection. Here the focus is on advective transfers between regions, since they are responsible for atmospheric transport.

The BETR North America model incorporates a generic vegetation compartment parameterized to represent the dominant vegetation type in each region (Cousins and Mackay, 2001). In general, diffusive exchange between air and vegetation is more rapid relative to plant death and litterfall than in the forest canopy model described by Wania and McLachlan, and the advective residence times for air in the regional environments are much shorter. As a result, the air–

vegetation–soil depositional pathway is not as efficient in “pumping” chemical from the atmosphere to the soil. However, when input parameters to the two models are harmonized, they give a similar description of the influence of vegetation on contaminant fate and transport.

Using the default parameters of the BETR North America model,  $Q_A$  has a value of approximately 1.03 for a chemical with  $\text{Log } K_{\text{ow}} = 7$ ,  $\text{Log } K_{\text{aw}} = -2.5$  and  $\text{Log } K_{\text{oa}} = 9.5$ . Therefore, including vegetation in the model does not significantly affect atmospheric concentrations, or the efficiency of long-range transport and deposition to the Great Lakes. Results from the BETR model are broadly consistent with the model of Severinsen and Jager (1998), who reported a theoretical maximum decrease in air concentrations of 40% ( $Q_A = 1.5$ ) in model scenarios that include vegetation compared with those that do not.

### 4. Time scale for atmospheric transport and deposition to the Great Lakes

In the results presented above it was assumed there was essentially no degradation of chemicals in the environment. Obviously Great Lakes Transfer Efficiency will be reduced if the substance degrades. Of greatest interest is how degradation in the atmosphere influences transfer efficiency, since transport through the atmosphere is the primary pathway to the Great Lakes. The key problem is assigning a time or half-life to the transport and deposition process ( $t_A$ ) that represents the atmospheric residence time between emission and deposition. This “transport time” can then be evaluated against the half-time for atmospheric degradation of the chemical and the extent to which degradation will reduce Great Lakes Transfer Efficiency determined. This is feasible because the BETR North America model uses first-order kinetics to describe all transport processes. If a competing degrading reaction with half-time  $t_R$  is introduced in the atmosphere in all regions of the model, the fraction of chemical that survives to deposit to the Lakes ( $F$ ), relative to a perfectly persistent chemical will be:

$$F = \frac{t_R}{t_R + t_A}$$

Justification for this lies in the observation that if the total process of transport and deposition to the Great Lakes and the process of degradation are characterized by first order rate constants  $k_A$  and  $k_R$ , then the total rate constant is  $(k_R + k_A)$ . The fraction reacted is then  $k_R/(k_R + k_A)$  and the fraction transported and deposited to the Lakes is  $k_A/(k_R + k_A)$ . Invoking the reciprocal relationship between rate constants ( $k$ ) and half-times ( $t$ ) gives the above relationship.

When  $t_R$  and  $t_A$  are equal,  $F$  is 0.5, and the Great Lakes Transfer Efficiency of the degrading chemical is half that of a perfectly persistent chemical with the same partitioning properties. The half-time for transport and deposition of a chemical to the Great Lakes can then be calculated by assuming illustrative atmospheric degradation half-lives of 1000 h ( $\sim 40$  days) for all chemicals and rearranging the above equation to give:

$$t_A = \frac{t_R(1 - F)}{F}$$

$F$  is calculated from the model output as the ratio of the GLTE of the degrading chemical to that of the perfectly persistent chemical.

Fig. 6 shows the half-times for transport and deposition to the Great Lakes for two representative chemicals for emissions to the atmosphere in each region of the BETR North America model. For both chemicals, transport times are longer as the chemical is transported over greater distances, as expected. Chemicals that are degraded in the atmosphere on a time scale that is more rapid than these transport times will be effectively prevented from reaching the Great Lakes, i.e., their atmospheric residence time from source to destination exceeds their reaction half-time.

Transport times from all regions for the semi-volatile chemical are longer than the corresponding times for the hydrophobic involatile chemical. This is attributable to relatively efficient removal of the hydrophobic involatile chemical from the atmosphere in all regions of the model by particle associated processes. This class of

chemical is virtually 100% associated with particles in the atmosphere at all environmental temperatures, and therefore it is efficiently removed by a combination of wet and dry particle deposition. Once deposited to the terrestrial surface volatilization is unlikely. Therefore, transport and deposition to the Great Lakes must occur on a time scale that is competitive with particle deposition processes. In contrast, the semi-volatile chemical is present primarily in the gas phase in the atmosphere, and may re-volatilize from the terrestrial surface after deposition. As a result, semi-volatile chemicals may remain in the atmosphere for a much longer time before depositing, and transport times are correspondingly longer.

The long transport times for semi-volatile chemicals imply that for a real chemical to have a GLTE that approaches that of a totally persistent chemical, it must be very resistant to degradation in the atmosphere, with a half-life of the order of weeks to months. Such a chemical might remain in the atmosphere for several days or weeks prior to being deposited to the lakes, and it may cycle between the atmosphere and the terrestrial surface between the point of release and the target ecosystem. An implication is that persistent semi-volatile chemicals do not require perfect meteorological conditions, i.e., winds that carry the chemical directly from the source region to the Great Lakes. They may follow an indirect route that covers a long distance, but ultimately brings the chemical into the Great Lakes Basin. This circuitous route is not available to the hydrophobic involatile chemical because it is scavenged from the atmosphere during the journey.

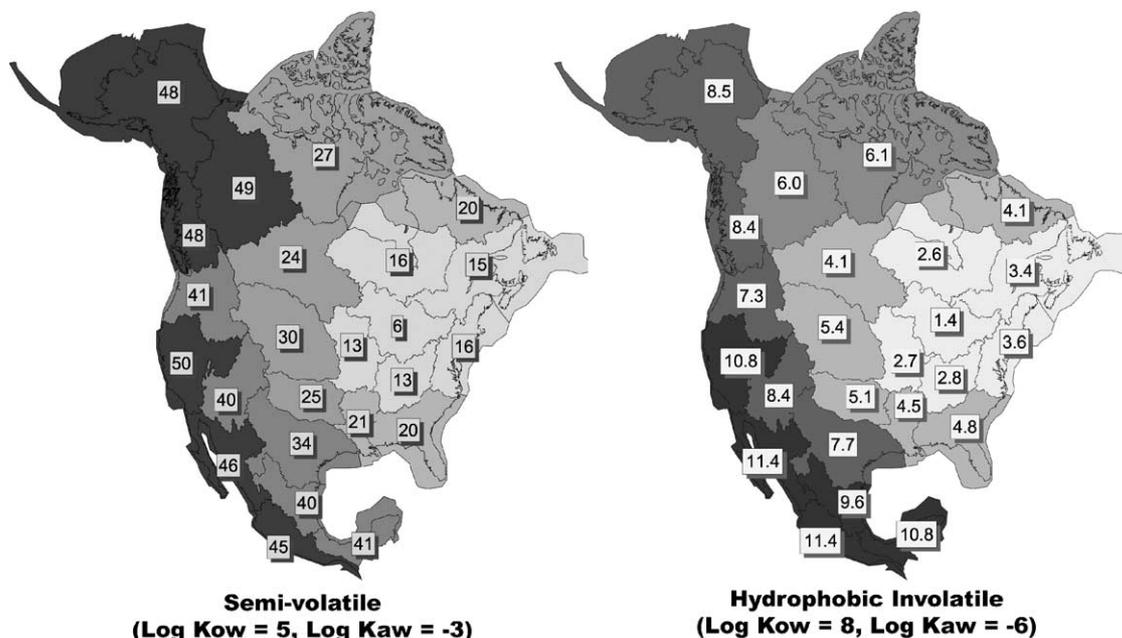


Fig. 6. Half-times (days) for transport and deposition of two representative hypothetical chemicals to the Great Lakes. Darker shaded regions indicate longer transport times.

## 5. Screening chemicals for high transfer efficiency

Trans-continental Great Lakes Transfer Efficiency follows a consistent pattern as a function of partitioning properties for organic chemicals, regardless of which region receives the primary emissions. Within each of the five partitioning classes indicated in Fig. 2 a single set of chemical fate and transport processes dominate the behavior of chemicals, and determine the efficiency with which they are transported and deposited. Efficient transport and deposition in the real environment not only requires appropriate partitioning properties, but also sufficient persistence in the atmosphere for a significant fraction of the chemical to make the journey from source region to receptor. However, classification of chemicals according to the scheme illustrated in Fig. 2 allows rapid identification of chemicals with potential for transport and deposition to the Great Lakes.

As an example we illustrate a screening-level assessment of GLTE of an “emerging” class of contaminants, the polybrominated diphenyl ethers (PBDEs) and compare them with the more thoroughly studied polychlorinated biphenyls (PCBs) and polychlorodibenzodioxins (PCDDs). Homologue groups of PCBs, PCDDs and PBDEs are plotted in Fig. 2. Partitioning properties for the PCBs and PCDDs are the recommended values of Mackay et al. (1999), those for PBDEs are calculated from the regression equations of Wania and Dugani (2003). For all three homologous series Log  $K_{ow}$  and chemical persistence increase with increasing halogenation of the parent compound, ie, the number of halogens on the parent molecule increases from left to right in the diagram. Several members of each homologous series fall in partitioning class 5, indicating moderate to high potential for continental-scale transport and deposition to the Great Lakes. Among the extremely hydrophobic members of each homologous series long-range transport and deposition to the Great Lakes is possible, but efficiencies of transport are low, occurring by particle-based processes.

Of particular interest are tetrabrominated diphenyl ethers (Log  $K_{ow}$   $\sim$ 6.3, Log  $K_{aw}$   $\sim$ -3.4, Log  $K_{oa}$   $\sim$ 10.3), which fall in partitioning class 5 and have sufficient Log  $K_{ow}$  to be bioaccumulative. PBDE 47, a tetrabrominated compound, is one of the most commonly detected PBDEs in environmental samples, and in contrast to PCBs and PCDDs, PBDE production and use is increasing in North America (Palm et al., 2002). The GLTE from the Mississippi Delta region for a totally persistent chemical with partitioning properties similar to PBDE 47 is 0.30% and the transfer time is 4.8 days. If  $t_A$  is 10.6 days, as has been estimated for PBDE 47 (Wania and Dugani, 2003), GLTE falls to 0.21%. In comparison, a perfectly persistent chemical with partitioning properties similar to toxaphene has a GLTE

from the Mississippi Delta region of 1.47% and a transfer time of 10 days. If  $t_A$  is 7.1 days, similar to toxaphene (MacLeod et al., 2001a), then the GLTE is 0.61%.

## 6. Discussion

Using a spatially explicit model of chemical fate in the North American environment we have identified combinations of physico-chemical properties that favor efficient transport and deposition to the Great Lakes, and estimated the time-scale required. Properties of historical contaminants that continue to cycle in the environment, such as PCBs, toxaphene and DDT, fall in ranges that are predicted to favor continental-scale transport and deposition to the Great Lakes. A classification scheme based on partitioning properties of chemicals is proposed, allowing rapid identification of the potential of existing and “new” chemicals such as the PBDEs for transport and deposition to the Lakes.

For an ecosystem to become contaminated from distant sources of chemicals two processes must occur; transport from the source region and deposition to the target ecosystem. Efficient transport and deposition to specific ecosystems is only possible for chemicals with certain combinations of partitioning properties and sufficient environmental persistence to survive the journey. The techniques outlined here and illustrated for the Great Lakes in a North American context could be applied to other ecosystems of concern, supported by an appropriate contaminant fate model. The same techniques could be applied using models based on political boundaries to assess the extent of trans-boundary migration of pollutants, and assess the relative impact of domestic and foreign sources of contaminants on regional environmental quality.

## Acknowledgements

Funding for this research was provided by Environment Canada and Health Canada through the Toxic Substances Research Initiative (TSRI), the Natural Sciences and Engineering Research Council (NSERC), and the consortium of companies that support the Canadian Environmental Modelling Centre at Trent University.

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